## COLOUR AND CHEMICAL CONSTITUTION.

Part XIV.—The Calculation of the Colour of the Dicyclic Dyes.

By James Moir.

The remarkable discovery published last year in the *Addendum* to Part X, whereby I was enabled to calculate the colour of methylene-blue from that of a dye containing neither nitrogen nor sulphur, has in the meantime proved very fertile. I have now worked out all the factors whereby the colour of any dye made up of *two* ionisable rings and either one or two linkages can be calculated. This means calculating quite two-thirds of the known dyes.

Dioxybenzhydrol, $HO \cdot C_6H_4 \cdot CH(OH) \cdot C_6H_4OH$ is an example of a singly-linked dicyclic dye, and dioxy-xanthhydrol
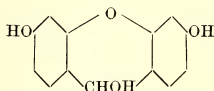
is an example of a doubly-linked dicyclic dye. Mono-oxybenzhydrol on the other hand is "monocyclic," having only one ionisable ring.

I find if the assumption is made that the wave-length of an electron-orbit going round *two* phenol rings is about λ 1380, that this orbit is *contracted* by linkage of the rings *always in the same proportion for the same linkage, whatever other groups are present.* Each linkage thus has a colour-factor (less than unity) which, when multiplied by 1380, gives the colour of the corresponding di-oxyphenyl-dye.

Table of Linkage Factors.

A. Methylene or	$/CH_2\backslash$	.	.	.	. Value 0·65.
B. Imino or	$/NH\backslash$	.	.	.	. Value 0·78.
C. Oxo- or	$/O\backslash$	.		.	. Value 0·89.
D. Thio- or	$/S\backslash$	.	.	.	. Value 0·92.

If *two* of the linkages are present in a phenolic dye, the figure 1380 is to be muliplied by *both* factors.

I have also discovered that the effect of oxidising the linkage is always the same whatever the linkage is. The effect is to make the factor of the oxidised linkage exactly $\frac{3}{5}$ of the factor of the unoxidised linkage.* This may be due, as explained in Part XII, to changing from five tautomerisms to three only.

Table of Factors for Oxidised Linkages.

E. Oxymethylene or carbinol linkage, ⟋CHOH⟍ Value 0·39

F. Dioxymethylene or keto linkage, ⟋ CO ⟍ Value 0·234

G. Oximino or hydroxylamine linkage, ⟋ NOH ⟍ Value 0·47

H. Peroxide linkage, ⟋ Ö ⟍ . . . . Value 0·535

I. Sulphoxide linkage, ⟋SO⟍ . . . . Value 0·55

J. Sulphone linkage, ⟋SO₂⟍ . . . . Value 0·33 (?)

[K. Trebly-linked carbinol, ≡ COH . . . Value 0·386]

These are all the *new* data required for the calculations, but in addition all of the 27 ring-colour-factors published in Part X may be used so as to extend the theory from the phenolic dyes to all sorts of classes of dicyclic dyes. Thus, for bis-dimethylamino dyes the figure for the corresponding phenolic dye is to be multiplied by the square of 1·059, the factor for replacement of OH by NMe_2 (Part X, p. 306, middle), or alternatively, instead of λ 1380, use λ $1380 \times (1·059)^2 = \lambda$ 1548 for the fundamental vibration round two dimethylaniline rings. Similarly the fundamental vibration for *two* aniline rings is λ $1380 \times \left(\dfrac{0·972}{0·9657}\right)^2$ or λ 1400 (Part X, p. 304).

According to this theory the colour of the majority of the *singly-linked* dicyclic substances, such as dioxydiphenylmethane, is in the infra-red : those which are observable to the eye are calculated below.

(1) *Dioxybenzhydrol* (formula on p. 65).—The calculated λ is $1380 \times$ factor E $= 1380 \times 0·39 = \lambda$ 538.   Observed λ 539.

(2) *Benzaurine* (di-para-variety).—This is the C-phenyl derivative of the foregoing. The C-phenyl factor is 1·026 (Part X, p. 310). Calculated λ $= 1380 \times 0·39 \times 1·026 = \lambda$ 552.   Observed λ 553.

(3) *Michler's hydrol.*—This is two dimethylaniline rings joined by CHOH.   Calculated $\lambda = 1548 \times 0·39 = \lambda$ 604.   Observed λ 603.

(4) *Malachite green.*—This is the C-phenyl derivative of No. 3. Calculated $\lambda = 1548 \times 0·39 \times 1·026 = \lambda$ 620.   Observed λ 619.

* Watson and Meek first showed this to be the case for the CO group.

(5) *Doebner's violet.*—This is No. 4 less four methyl groups. Calculated $\lambda = 1400$ (see 15 lines above) $\times\ 0.39 \times 1.026 = \lambda\ 561$. Observed $\lambda\ 562$.

(6) *Aurine.*—Here the linkage K is used instead of linkage E, although they are nearly the same. As shown in Part XII, p. 209, only two of the three rings act in producing the colour. The calculated λ is $1380 \times 0.386 = \lambda\ 533$. Observed $\lambda\ 534$.

(7) *Fuchsine (para).*—Two aniline rings and the factor K are used. Calculated $\lambda = 1400 \times 0.386 = \lambda\ 541$. Observed $\lambda\ 543$. Commercial fuchsine has an extra C-methyl group and has $\lambda\ 549$. Calculated, using the C-methyl factor $1.012 = \lambda\ 547$.

(8) *Crystal violet.*—Two dimethylaniline rings and factor K to be used. Calculated $1548 \times 0.386 = \lambda\ 597$. Observed $\lambda\ 595$.

(9) *Aniline blue.*—Two diphenylamine groups and the factor K to be used. The N-phenyl factor has twice the effect of the C-phenyl factor (*cf.* ortho- and meta- groups in Part IV, p. 188). Its value is therefore $(1.026)^2 = 1.054$. Hence two diphenylamine groups have the value $\lambda\ 1400 \times (1.054)^2 = \lambda\ 1554$, and the calculated value for aniline blue is $1554 \times 0.386 = \lambda\ 599$. Observed $\lambda\ 600$.

(10) *Phenolphthalein.*—This is No. 1 with a benzoic acid group attached. The factor for the latter is C-phenyl multiplied by *o*-carboxyl (see Part X, p. 306) $= 1.026 \times 1.002 = 1.028$. Calculated λ for phenolphthalein $= 1380 \times 0.39 \times 1.028 = \lambda\ 553$. Observed $\lambda\ 554$.

(11) *Phenolsulphonephthalein.*—This is No. 1 plus a benzenesulphonic acid group. The latter's factor is 1.026×1.018 (Part X, p. 308) $= 1.045$. The calculated λ is $1380 \times 0.39 \times 1.045 = \lambda\ 562$. Observed $\lambda\ 563$.

(12) *Michler's ketone.*—Two dimethylaniline rings and the factor F are to be used. Calculated $\lambda\ 1548 \times 0.234 = \lambda\ 362$. Observed $\lambda\ 364$.

(13) *Indophenol.*—This is the anhydride of dioxy-diphenylhydroxylamine.* Two phenol rings and the factor G are therefore to be used. Calculated $\lambda = 1380 \times 0.47 = \lambda\ 649$. Observed $\lambda\ 650$.

(14) *Indamine.*—This in the same way is derived from two aniline rings and the factor G. Calculated $\lambda = 1400 \times 0.47 = \lambda\ 658$. Observed $\lambda\ 660$.

(15) *Bindschedler's green.*—This is tetramethylindamine, and the calculation requires two dimethylaniline rings and the factor $G = \lambda\ 1548 \times 0.47 = \lambda\ 728$. Observed $\lambda\ 730$.

Doubly-linked Dicyclic Colours.

Of these there is an enormous number in use, varying from eosine to safranine and methylene-blue. If all the ten factors were used two at a time there would be 100 colours of each of the three classes, viz. phenols, anilines and dimethylanilines. I therefore limit myself to those I have observed, or for which *data* exist in the literature.

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* Commercial "indophenol" is a naphthol compound.

(16) *Pyronine.*—This has the formula :
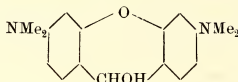
It is calculated by multiplying $\lambda\,1548$ (for the dimethylaniline rings) by factors C and E, viz. $1548 \times 0\cdot89 \times 0\cdot39 = \lambda\,536$. Observed $\lambda\,542$ in alcohol.

(17) *Rhodamine.*—This is the benzoic-acid derivative of pyronine (*cf.* phenolphthalein). The benzoic factor is $1\cdot028$ (see p. 67). The calculated λ is $536 \times 1\cdot028 = \lambda\,552$. Observed $\lambda\,553$.

(18) *Dioxyxanthhydrol.*—This is pyronine with 2OH instead of 2NMe_2. Calculated $1380 \times 0\cdot89 \times 0\cdot39 = \lambda\,478$. Observed $\lambda\,479$. This substance is the parent of fluorescein.

(19) *Fluorescein.*—The above plus benzoic acid is fluorescein. Calculated $478 \times 1\cdot028 = \lambda\,492$. Observed $\lambda\,494$.

(20) *Eosine.*—This is fluorescein plus four ortho-bromines. Calculated $\lambda = 492 \times (1\cdot0128)^4$ (see Part IX) $= \lambda\,519$. Observed $\lambda\,521$.

(21) *Resorufine.*—This has the formula :
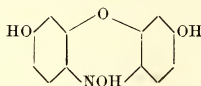
$\lambda\,1380$ for the phenol rings is therefore multiplied by factors C and G. The result is $1380 \times 0\cdot89 \times 0\cdot47 = \lambda\,577$. Observed $\lambda\,576$.

(22) *Thionol.*—This is the foregoing with S in place of O. The calculated value is $1380 \times 0\cdot92 \times 0\cdot47 = \lambda\,597$. Observed $\lambda = 593$.

(23) *Methylene-blue.*—This is the example given in the *Addendum* to Part X. It is thionol with two dimethylaniline rings instead of two phenol rings. Calculated $1548 \times 0\cdot92 \times 0\cdot47 = \lambda\,668$. Observed $\lambda\,665$. Formánek gives $\lambda\,667\frac{1}{2}$ in what was probably a better specimen.

(24) *Thionine.*—This has the formula :
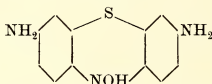
Calculated value $= 1400$ (for two aniline rings) $\times 0\cdot92 \times 0\cdot47 = \lambda\,604$. Observed $\lambda\,603$.

(25) *Gentianine.*—This is halfway between Nos. 23 and 24 in constitution. Since the scheme is factorial its calculated λ is the geometric mean (not the arithmetical mean) of the $\lambda\lambda$ of Nos. 23 and 24 $= \lambda\,635$. Formánek observed $\lambda\,638$.

(26) *Dioxyacridine.*—This can be written in four ways and calculated from either of the hydrated forms, viz.:

(a)

(b)

(c)

(d)
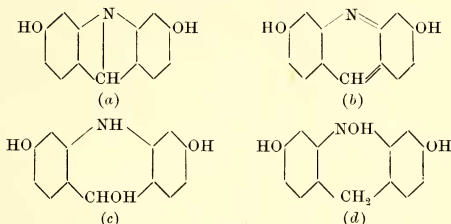
According to formula (*c*) it is dioxybenzhydrol with the NH linkage: calculated $1380 \times 0.39 \times 0.78 = \lambda\ 420$.

According to formula (*d*) the calculation is $1380 \times 0.65 \times 0.47 = \lambda\ 422$. The difference is due merely to the factors not yet being accurately known to three places of decimals. Observed $\lambda\ 421$.

(27) *Benzoflavine.*—This has the formula:
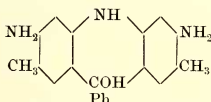
The calculation involves $\lambda\ 1400$ for the two aniline rings, multiplied by (*a*) the CHOH factor, (*b*) the NH factor, (*c*) the phenyl factor, (*d*) the square of the orthomethyl factor (see example No. 7). The calculated value is $1400 \times 0.39 \times 0.78 \times 1.026 \times (1.012)^2 = \lambda\ 449$. The observed value was about $\lambda\ 454$.

(28) *Dioxyphenazine.*—This, being symmetrical, has only two formulæ, viz.:

 and
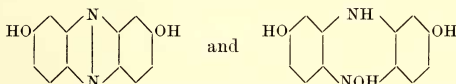
Its calculated λ is $1380 \times 0.78 \times 0.47 = \lambda\ 506$. Observed $\lambda\ 510$.

(29) *Neutral red.*—This is dimethyldiamino-toluphenazine. The parent rings are one aniline and one dimethylaniline ring, the value of which (see No. 25) is $\sqrt{1400 \times 1548} = \lambda\ 1473$. This is to be multiplied by the NH and NOH factors and by 1.012 for the ortho-methyl group (see No. 27). Calculated $\lambda\ 546$. Observed $\lambda\ 540$ (commercial specimen).

(30) *Safranine.*—This has the formula (when hydrated):
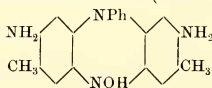
Calculated $\lambda = 1400 \times 0.78 \times 0.47 \times 1.026$ (for phenyl) $\times (1.012)^2$ (= benzo-flavine $\times 0.47 \div 0.39$) = $\lambda 541$. Observations in commercial specimens vary between $\lambda 530$ and $\lambda 540$; probably some do not contain the methyl groups.

(31) *Methylene violet.*—This is isomeric with safranine, but the two methyls are on nitrogen not in the ring. Calculated 1473 (see No. 29) $\times 0.39 \times 0.78 \times 1.026 = \lambda 554$. Commercial specimens vary in observation between $\lambda 550$ and $\lambda 565$, being mixtures. Another way of calculating this isomeric substance is to note that the N-methyl group has twice the effect of the C-methyl group, the latter having a factor of 1.012 ; the former has a factor of $(1.012)^2 = 1.0245$ (see Part X, p. 305). Consequently No. 31 calculated from No. 30 is $\lambda 541 \times (1.0245)^2 \div (1.012)^2 = \lambda 541 \times (1.012)^2 = \lambda 554$. This doubling of effect on changing from C-substitution to N-substitution has already been mentioned under substance No. 9, but it is to be noted that phenyl (and probably methyl also) *on a linkage* has always the value 1.026 whether on C or on N.

(32) *Magdala red.*—This is safranine with two naphthalene-rings attached, and a third in the linkage instead of phenyl. The calculated colour of phenyldiaminophenazonium salts is $\lambda 527$, whereas Magdala red shows $\lambda 559$. Assuming that the linkage-naphthyl has the same effect as phenyl, this gives a factor of 1.030 for the naphthalene-ring residues, each C_4H_4. This is a much smaller value than that found from the naphthol-phthaleins (1.092), and remains an anomaly until further work can be done on naphthalene colours in general.*

(33) *Azine green.*—This is about the most complicated member of the series. It has the formula :
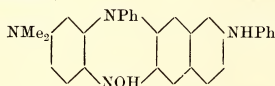
As shown under No. 32, phenyldiaminophenazonium has $\lambda 527$. Azine-green has, in addition to the latter, a naphthalene-ring, two N-methyls and one N-phenyl (value 1.054). Assuming naphthalene to have the normal value of 1.09, because the amino group is *outside* it in this case, the calculated colour of azine-green is $527 \times (1.0245)^2 \times 1.054 \times 1.09 = \lambda 636$. I have not observed it, but the description in the literature indicates that the observed value lies between $\lambda 620$ and $\lambda 640$.

(34) *Dioxyanthracene.*—The ordinary formula of this substance when written hydrated becomes :
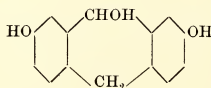
* Since this was written it has been discovered that naphtholphthalein has ortho linkages instead of para as hitherto supposed. There is thus no anomaly after all.

The calculated colour is $1380 \times 0.65 \times 0.39 = \lambda\,350$. It is described in 'Beilstein' as pale yellow, which agrees with the calculation. Dioxydihydro-anthracene should have a deeper colour corresponding to $1380 \times (0.65)^2 = \lambda\,583$.

Dioxyanthraquinone is an exception : the two CO groups cause a new kind of vibration, and the colour is much higher—eight times as high in fact as theory predicts. No doubt the theoretical colour ($\lambda\,76$) is there also, but is too low to observe.

These nineteen doubly-linked dicyclic colours have been selected so as to cover the whole field, so far as known (the peroxide and sulphoxide dyes are not yet known) : it would merely be taking up space, for example, to calculate erythrosine when eosine is calculated, or to calculate the fourteen derivatives of thionine observed by Formánek.

There are also dicyclic dyes in which the rings are joined by chains longer than one element : indigo and the azo-dyes are examples, but the published *data* are insufficient—indeed almost useless—as regards a quantitative explanation.

Indigo may be calculable from the hydrated formula :

$$\text{—CO—C(OH) : C(OH)—CO—} \quad \text{(NH}_2\text{)}$$
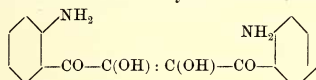
and the thiazole and primuline dyes similarly, viz. :

$$\text{—S—CO—}\quad\text{NH}_2$$
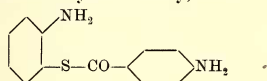
but the laws of the co-operation of two or more factors *in a linkage* are not yet known. The azo-dyes do not come into the scheme for the reason that they are coloured whether they contain ionisable groups or not ; but it is worth noting that the three which *do* contain two ionisable rings (azophenol, azoaniline, etc.) have colours fairly similar to those of the corresponding phenazines, from which they differ by two hydrogen atoms only. This suggests that the azo group can sometimes be written —NH—NOH— and the colour calculated accordingly, allowing about 0.73 instead of 0.78 for the $\diagup$NH$\diagdown$ factor when not replacing two hydrogen atoms of the benzene rings but inserted in a previously existing linkage.

The most of the azo-dyes, however, owe their colour to the azo-linkage independently of all rings, since diazomethane shows colour.

It is probably desirable to show the way in which the linkage-factors were ascertained from the observations, particularly as this also exhibits the degree of variation of each factor, and enables the reader to see that each factor is really a constant within the observational error.

(1) *The oxo-linkage.*—(*a*) Resorcin-benzene : observed $\lambda\,492$. The corre-

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sponding substance without the oxo-linkage is benzaurine, which has λ 553. Oxo-linkage-factor from (*a*) = 492 ÷ 553 = 0·890.

(*b*) Fluorescein = λ 494 : corresponding substance = phenolphthalein of λ 554. Oxo-factor = 494 ÷ 554 = 0·892.

(*c*) Eosine = λ 521, whereas tetrabromophenolphthalein has λ 584. Oxo-factor = 521 ÷ 584 = 0·892.

(*d*) Resorcin-sulphophthalein = λ 498, compared with phenolsulphophthalein of λ 563 gives the oxo-factor = 0·885.

(*e*) The tetrabromo-derivatives (3–3′–5–5′) of the foregoing two substances have λ 527 for the resorcin compound and 594 for the phenol compound. The oxo-factor in this case is 0·887.

(*f*) Pyronine has λ 542 in alcohol, and Michler's hydrol has λ 610 in the same solvent. The oxo-factor in this case is 0·889.

(*g*) Dioxyxanthhydrol has λ 479 in water, and dioxybenzhydrol λ 539. The oxo-factor for this pair is thus 0·888.

(*h*) Tetramethyl-rhodamine has λ 553 (same as benzaurine). The corresponding substance without the oxo-linkage is "dimethylanilinphthalein," which I have not observed. It is related to malachite green just as phenolphthalein λ 554 is to benzaurine λ 553, therefore its λ must be that of malachite green plus 1 = λ 620. Hence the oxo-factor for this pair is 553 ÷ 620 = 0·892.

(*i*) Resorufine has λ 576 : the substance without the oxo-linkage is indophenol of λ 650. The oxo-factor here is 0·887.

(*j*) Hexabromo-derivatives of fluorescein and phenolphthalein substituted in the same six places (*acfgjk* of Part XI) have λλ 535 and 602 respectively. The oxo-factor from this pair is 0·889.

(*k*) Isomeric hexabromo-derivatives derived from 3–6 dibromophthalic acid (*adfgjk* of Part XI) have λλ 538 and 606 respectively. This oxo-ratio is 0·888.

The average of these eleven observations gives 0·889 for the oxo-ratio, but I am of opinion that much more weight should be given to those depending on common substances, and that consequently the true value is 0·891.

(2) *The thio-linkage.*—This could be derived from as many substances as the oxo-factor, but the substances, thiofluorescein, thiopyronine, etc., are not obtainable or capable of being made here. I have therefore calculated it from the methylene-blue and thionol classes alone :

(*a*) Methylene-blue and Bindschedler's green have λλ 665 and 730 respectively. The ratio is 0·912.

(*b*) Thionine and indamine have λλ 603 and 660 respectively. The ratio is 0·915.

(*c*) Thionol and indophenol have λλ 593 and 650 respectively. The ratio is 0·913.

I hope that some one will examine the thioxanthhydrol dyes, and thus enable the thio-factor also to be stated to three places of decimals.

(3) *The imino-linkage.*—The acridine dyes are NH-derivatives of the benzhydrol dyes : similarly the phenazines are related to the indophenols.

(*a*) Flavine (diaminoacridine) has λ about 427, whilst diaminobenzhydrol has λ 548. The NH ratio is here 0·780.

(*b*) Benzoflavine A (substance No. 27 without the methyl-groups) has λ about 450 (broad). The corresponding substance without the NH group is Doebner's violet, which has λ 562. The NH ratio is here 0·80. This, being exceptional, is probably wrong. The acridine dyes analogous to the phthaleins and rhodamines appear to be little known, and are inaccessible here ('Beilstein,' iv, supplement, p. 879. Calculated λ 438.)

(*c*) Bisdimethylamino-phenazine has λ about 565, and Bindschedler's green λ 730. The NH ratio is here 0·774.

(*d*) Dioxyphenazine has λ about 510 (broad), and indophenol λ 650. The NH ratio is here 0·785.

(*e*) Safranine (without methyl groups) has λ 525 compared with indamine λ 660, giving 0·796 for the NPh ratio, whence NH is $0·796 \div 1·026 = 0·778$.

(4) *The methylene-linkage.*—This is inferred from the acridine dyes, this time compared with the indophenols, on the principle that when two linkages are present it does not matter which is the oxidised one, *i.e.* $(CH_2 + NOH) = (CHOH + NH)$.

(*a*) Flavine / indamine $= 427 / 660$. Value of $\diagup CH_2 \diagdown = 0·647$.

(*b*) Dioxyacridine / indophenol $= 421 / 650$. Value of $\diagup CH_2 \diagdown = 0·649$.

The oxidised factors.—Here the supposition is made that since a factorial scheme has been shown to be generally successful, and since Watson and Meek have established the factor $\frac{3}{5}$ for the change of linkage from CHOH to CO, this factor $\frac{3}{5}$ will also hold for any other oxidation of the linkage. Hence the value of $\diagup CHOH \diagdown$ is $\frac{3}{5}$ of $\diagup CH_2 \diagdown = 0·39$, and $\diagup NOH \diagdown = \frac{3}{5}$ of 0·78, and so on. That this supposition is correct is proved by the consistency of the results given in this paper.

The next step is to calculate the colour of the unobservable singly-linked dicyclic substances :

(1) *Dioxy-phenyl ether.*—This is (1) dioxyxanthhydrol less CHOH : calculated $\lambda 479 \div 0·39 = \lambda 1229$, (2) resorufine less NOH : calculated $\lambda 576 \div 0·468 = \lambda 1230$.

(2) The calculation for the sulphur-ether *dioxyphenylsulphide* gives $\lambda 1258$.

(3) *Dioxy-diphenylamine.*—This from dioxyphenazine is calculated to have $\lambda 510 \div 0·468 = \lambda 1090$: from dioxyacridine the calculated value is $\lambda 421 \div 0·39 = \lambda 1080$: from resorufin $\lambda 576 \div (\frac{3}{5}$ of $0·891) = \lambda 1077$ and so on.

(4) *Dioxy-diphenylmethane.*—This from dioxyacridine is calculated to

have $\lambda\,421 \div 0\cdot468 = \lambda\,900$: from dioxyxanthhydrol and the fluoresceins rather less : the average is $\lambda\,898$.

The final triumph of the scheme comes when it is found that the wavelengths of the seven singly-linked substances are themselves related to a fundamental constant (about 1380) by means of the factors contained in themselves :

Dioxy-phenyl ether, $\lambda\,1230$, divided by the $/\mathrm{O}\backslash$ factor $0\cdot891$, gives 1382.

Dioxy-diphenylamine, $\lambda\,1083$, divided by the $/\mathrm{NH}\backslash$ factor $0\cdot78$, gives 1388.

Dioxy-diphenylmethane, $\lambda\,898$, divided by the $/\mathrm{CH_2}\backslash$ factor $0\cdot65$, gives 1382.

Dioxy-benzhydrol, $\lambda\,539$, divided by the $/\mathrm{CHOH}\backslash$ factor $0\cdot39$, gives 1381.

Indophenol, $\lambda\,650$, divided by the $/\mathrm{NOH}\backslash$ factor $0\cdot47$, gives 1383.

Dioxy-phenylsulphide, $\lambda\,1258$, divided by the $/\mathrm{S}\backslash$ factor $0\cdot92$, gives 1370.

Dioxy-benzophenone, λ about 323, divided by the $/\mathrm{CO}\backslash$ factor $0\cdot234$, gives 1380.

This makes it almost certain that the unobserved ones have really the absorption-bands in the infra-red calculated in this paper.